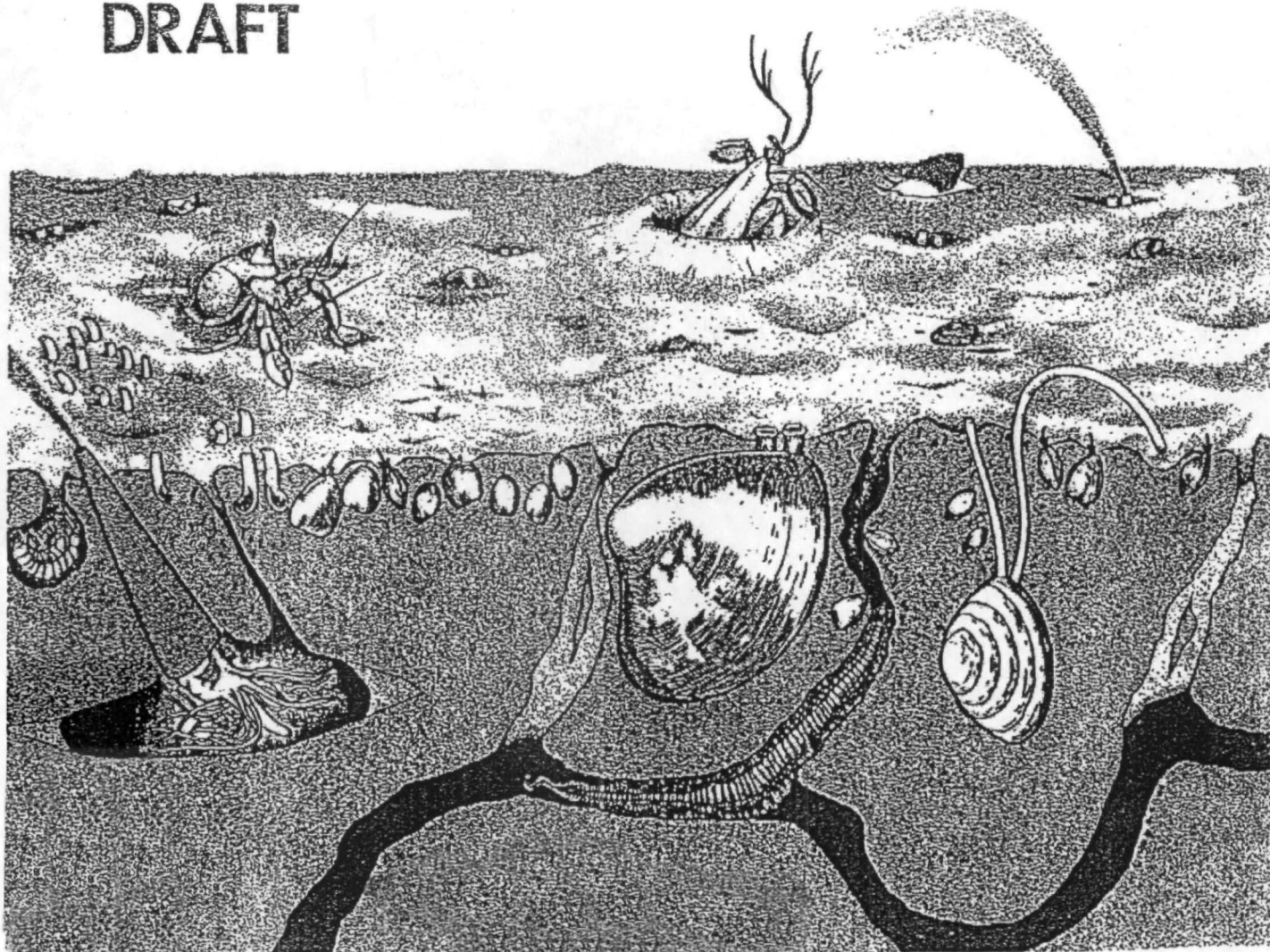




Methods for the Derivation of Site-Specific Equilibrium Partitioning Sediment Guidelines (ESGs) for the Protection of Benthic Organisms: Nonionic Organics

DRAFT



Foreword

Under the Clean Water Act (CWA), the U.S. Environmental Protection Agency (EPA) and the States develop programs for protecting the chemical, physical, and biological integrity of the nation's waters. To meet the objectives of the CWA, EPA has periodically issued ambient water quality criteria (WQC) beginning with the publication of "Water Quality Criteria, 1972" (NAS, 1973). The development of WQC is authorized by Section 304(a)(1) of the CWA, which directs the Administrator to develop and publish "criteria" reflecting the latest scientific knowledge on (1) the kind and extent of effects on human health and welfare, including effects on plankton, fish, shellfish, and wildlife, that may be expected from the presence of pollutants in any body of water, including ground water; and (2) the concentration and dispersal of pollutants on biological community diversity, productivity, and stability. All criteria guidance through late 1986 was summarized in an EPA document entitled "Quality Criteria for Water, 1986" (U.S. EPA, 1987). Updates on WQC documents for selected chemicals and new criteria recommendations for other pollutants have been more recently published as "National Recommended Water Quality Criteria-Correction" (U.S. EPA, 1999). EPA will continue to update the nationally recommended WQC as needed in the future.

In addition to the development of WQC and to continue to meet the objectives of the CWA, EPA has conducted efforts to develop and publish equilibrium partitioning sediment guidelines (ESGs) for some of the 65 toxic pollutants or toxic pollutant categories. Toxic contaminants in bottom sediments of the nation's lakes, rivers, wetlands, and coastal waters create the potential for continued environmental degradation even where water column contaminant levels meet applicable water quality standards. In addition, contaminated sediments can lead to water quality impacts, even when direct discharges to the receiving water have ceased. These guidelines are authorized under Section 304(a)(2) of the CWA, which directs the Administrator to develop and publish information on, among other things, the factors necessary to restore and maintain the chemical, physical, and biological integrity of all navigable waters.

The ESGs and associated methodology presented in this document are EPA's best recommendation as to the concentrations of a substance that may be present in sediment while still protecting benthic organisms from the effects of that substance. These guidelines are applicable to a variety of freshwater and marine sediments because they are based on the biologically available concentration of the substance in the sediments. These ESGs are intended to provide protection to benthic organisms from direct toxicity due to this substance. In some cases, the additive toxicity for specific classes of toxicants (e.g., metal mixtures or polycyclic aromatic hydrocarbon mixtures) is addressed. The ESGs do not protect against synergistic or antagonistic effects of contaminants or bioaccumulative effects to benthos. They are not protective of wildlife or human health endpoints.

EPA recommends that ESGs be used as a complement to existing sediment assessment tools, to help assess the extent of sediment contamination, to help identify chemicals causing toxicity, and to serve as targets for pollutant loading control measures. EPA is developing guidance to assist in the application of these guidelines in water-related programs of the States and this Agency.

This document provides guidance to EPA Regions, States, the regulated community, and the public. It is designed to implement national policy concerning the matters addressed. It does not, however, substitute for the CWA or EPA's regulations, nor is it a regulation itself. Thus, it cannot impose legally binding requirements on EPA, States, or the regulated community. EPA and State decisionmakers retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance where appropriate. EPA may change this guidance in the future.

This document has been reviewed by EPA's Office of Science and Technology (Health and Ecological Criteria Division, Washington, DC) and Office of Research and Development (Mid-Continent Ecology Division, Duluth, MN; Atlantic Ecology Division, Narragansett, RI; Western Ecology Division, Corvallis, OR), and approved for publication.

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Executive Summary

The purpose of this document is to provide guidance on procedures that can be used to modify national equilibrium partitioning sediment guidelines (ESGs) for nonionic organic chemicals to reflect specific local conditions. This methodology is issued in support of the published ESGs for endrin and dieldrin (U.S. EPA, 2000a,b) and is intended to supplement the procedures described for calculating ESGs for nonionic organic chemicals based on the equilibrium partitioning (EqP) theory as described in the ESG Technical Basis Document (U.S. EPA, 2000c).

According to the EqP theory, a nonionic chemical in sediment partitions between sediment organic carbon, interstitial (pore) water, and benthic organisms. At equilibrium, if the concentration in any one phase is known, then the concentration in the others can be predicted. The ratio of the concentration in water to the concentration in sediment organic carbon is termed the organic carbon partition coefficient (K_{OC}), which is a constant for each chemical. It has been demonstrated that if the effect concentration in water is known, for example, a water quality criteria final chronic value (WQC FCV), the effect concentration in sediments on an organic carbon basis (ESG_{OC}) can be accurately predicted by multiplying the effect concentration in water by the chemical's K_{OC} (U.S. EPA, 2000c).

The U.S. Environmental Protection Agency (EPA) currently recognizes that the national ESGs may be under- or overprotective when (1) pertinent differences occur between the sensitivities of benthic organisms at a site and the organisms used to derive the WQC FCV, or (2) differences occur in the bioavailability of the chemical in the sediment from the site because of alternate partitioning phases or the presence in the sediment of undissolved chemical. The two procedures recommended to correct for such site-specific differences are the Resident Species Deletion/Substitution Procedure (U.S. EPA, 1994) and the Bioavailability Procedure. The basic principle of the Resident Species Deletion/Substitution Procedure is to permit deletion of all acute values for nonresident benthic species/life-stages and water column species/life-stages when acute values for all benthic resident species/life-stages in a family have been tested. The Bioavailability Procedure assumes that the true concentration of bioavailable chemical can be reasonably measured or estimated as freely-dissolved chemical in interstitial water, which can then be compared with the WQC FCV. For the latter value, sediments in which the freely-dissolved interstitial water concentration is less than the WQC FCV are acceptable for maintaining the presence of benthic organisms. If bioassays demonstrate that a sediment is toxic, EPA recommends sediment-specific risk assessments. These risk assessments should utilize a tiered approach prior to conducting the site-specific ESG modification procedures to identify chemicals causing the observed effects (such as a Toxicity Identification Evaluation [TIE]) (e.g., Ankley et al., 1991; Ho et al., 1997).

Glossary of Abbreviations

ACR	Acute-chronic ratio
ASTM	American Society for Testing and Materials
C_d	Freely-dissolved interstitial water chemical concentration
C_{TW}	Total interstitial water chemical concentration
CWA	Clean Water Act
DOC	Dissolved organic carbon
EPA	United States Environmental Protection Agency
EqP	Equilibrium partitioning
ESA	Endangered Species Act
ESG(s)	Equilibrium partitioning sediment guideline(s)
ESG _{OC}	Organic carbon-normalized equilibrium partitioning sediment guideline
ESG _{OC,SS}	Site-specific organic carbon-normalized equilibrium partitioning sediment guideline
FACR	Final acute-chronic ratio
FACR _{SS}	Site-specific final acute-water chronic ratio
FAV	Final acute value
FAV _{SS}	Site-specific final acute value
FCV	Final chronic value
FCV _{SS}	Site-specific final chronic value
GC/MS	Gas chromatograph/mass spectrophotometer
GMAV	Genus mean acute value
HECD	U.S. EPA, Health and Ecological Criteria Division
K_{DOC}	Dissolved organic carbon-water partition coefficient
K_{OC}	Organic carbon-water partition coefficient
K_{OW}	Octanol-water partition coefficient
L-L	Liquid-liquid extraction
NAS	National Academy of Sciences
NTIS	National Technical Information Service

Section 1

Purpose and Application

1.1 General Information

The purpose of this document is to provide guidance on procedures that can be used to modify national equilibrium partitioning sediment guidelines (ESGs) for nonionic organic chemicals to reflect local environmental conditions. These procedures may be utilized as part of the basis for establishing site-specific sediment quality standards to protect the uses of a specific water body. The procedures are intended to apply to the sediment guidelines for endrin and dieldrin (U.S. EPA, 2000a,b) and ESGs published for other substances including, but not limited to, mixtures of metals (cadmium, copper, lead, nickel, silver, and zinc) (U.S. EPA, 2000f) and mixtures of polycyclic aromatic hydrocarbons (PAHs) (U.S. EPA, 2000g).

A thorough understanding of the "Technical Basis for the Derivation of Equilibrium Partitioning Sediment Guidelines (ESGs) for the Protection of Benthic Organisms: Nonionic Organics" (U.S. EPA, 2000c), the ESG documents for endrin and dieldrin (U.S. EPA, 2000a,b), "Implementation Framework for Use of Equilibrium Partitioning Sediment Guidelines (ESGs)" (U.S. EPA, 2000d), "Interim Guidance on Determination and Use of Water-Effect Ratios for Metals" (U.S. EPA, 1994), "Water Quality Standards Handbook" (U.S. EPA, 1983), "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses" (Stephan et al., 1985), response to public comment on the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses" (U.S. EPA, 1985), and the response to public comment on the proposed ESGs (U.S. EPA, 2000e) is recommended. Importantly, these procedures for site-specific modification of national ESGs should be used only after expanded chemical monitoring of chemical concentrations in sediments and interstitial water; biological monitoring including toxicity tests, TIEs, and faunal surveys; and other risk assessment procedures that have been conducted at the specific site, preferably using a tiered approach.

The national ESGs have been developed specifically for use in the 304(a) criteria program. These guidelines are EPA's best estimate of the highest

concentration of a substance in sediments that will protect benthic (infaunal and epibenthic) organisms including macroinvertebrates and fishes.

The U.S. EPA, Office of Science and Technology (OST), recognizes and has encouraged the potential use of sediment guidelines by other EPA programs. Appropriate use of the site-specific ESG in these programs should be obtained from the implementation guidance developed by that program for inclusion in the "Implementation Framework for Use of Equilibrium Partitioning Sediment Guidelines (ESGs)" (U.S. EPA, 2000d).

1.2 Rationale for Procedures Used to Develop Site-Specific Guidelines

National ESGs may be under- or overprotective if (1) the benthic (infaunal and epibenthic) species at the site are more or less sensitive than the benthic and water column species included in the national criteria dataset or (2) the sediment or chemical quality characteristics at the site alter the bioavailability and, consequently, the toxicity of the sediment-bound chemical relative to that predicted by the equilibrium partitioning (EqP) theory. Therefore, it is appropriate that site-specific guidelines procedures address each of these conditions.

This document recommends the use of the Resident Species Deletion/Substitution Procedure to adjust the national ESG for the sensitivity of species found at the site. It is similar to the Recalculation Procedure published for use as a means to modify national water quality criteria (WQC) values (U.S. EPA, 1983, 1994). This approach permits deletion of certain toxicological data on (1) water column species, (2) nonresident benthic species, and (3) water column life-stages of a resident species having both benthic and water column life-stages. For example, although water column species have sensitivities similar to those of benthic species overall (Di Toro et al., 1991), sensitivities of water column species at a site may differ from those of benthic species found there. The toxicological data on these species may not be applicable to the derivation of a site-specific guideline;

therefore, these data can be deleted. Furthermore, the national criteria dataset may contain data for benthic fauna that are particularly sensitive (e.g., certain amphipods, penaeid shrimp, or mysids) or insensitive (e.g., certain adult polychaetes or molluscs) to some chemicals. If they do not occur at a particular site, their sensitivities may not be representative of those species expected to be found there, and toxicological data on them can be deleted. When resident organisms such as echinoderms, molluscs, or crustaceans have both benthic and water column life-stages, and both have been tested, data from tests with the benthic life-stage are most relevant to the site-specific ESG, and data on water column life-stages can be deleted. When nonresident benthic species or water column life-stages of resident species having a benthic life-stage are likely to be toxicologically related to untested resident benthic species because of their taxonomic relationship, deletion of acute toxicity data on them is prohibited. However, it should be noted that deletion of toxicological data may result in loss of taxonomic representation required to meet the minimum database for deriving WQC (Stephan et al., 1985). These WQC are used to derive the national ESG. For this reason, additional testing may be required. Furthermore, given the rules of this procedure, EPA strongly encourages that additional tests be conducted with resident benthic species to permit replacement of data on surrogate species or life-stages.

This document recommends the use of the Bioavailability Procedure as a means to replace the national ESG when there are differences in the bioavailability of the chemical in unique sediments. These unique sediments can be identified by measuring the chemical both in sediment and dissolved in interstitial water, then comparing the resultant partition coefficient with the organic carbon partition coefficient (K_{OC}) in the sediment guidelines document. Through use of this procedure, the bioavailability concentration of the chemical in interstitial water can be quantified for comparison to the WQC final chronic value (FCV) found in the chemical-specific ESG documents for nonionic organic chemicals.

The reason for using the Bioavailability Procedure is that, although a variety of sediments have been tested that demonstrate the applicability of the EqP approach to a wide array of sediments (U.S. EPA, 2000c), at certain unique sites sediments do exist where EqP theory does not accurately predict partitioning. Unique sediment characteristics, chemical speciation, or chemical form may make the guidelines chemical more or less bioavailable, thereby altering the toxicity

of the sediment (for further detail, see Section 4.1.3 in the Technical Basis Document [U.S. EPA, 2000c]). For example, in some sediments the partitioning of PAHs cannot be explained by standard models of equilibrium partitioning to organic carbon (Maruya et al., 1996; McGroddy et al., 1996). Instead, accurate predictions of partitioning behavior may require the use of both a K_{OC} and a soot carbon partition coefficient (Gustafson et al., 1997). Quantification of partitioning at these sites requires measurement of the concentration of the nonionic organic chemical in interstitial water and sediment.

In cases where it is necessary to identify causative chemicals when toxicity is indicated by bioassays or other tools, EPA recommends sediment-specific risk assessments be conducted using a tiered approach. This assessment may include expanded monitoring of chemical concentrations in sediments and interstitial water; biological monitoring including toxicity tests and faunal surveys (Swartz et al., 1994), and TIEs (Ankley et al., 1991; Ho et al., 1997); and other risk assessment procedures conducted at the specific site. These studies are recommended prior to conducting the site-specific ESG modification procedures to identify chemicals causing observed effects and partitioning not predicted by EqP theory. In the context of the tests used in this risk assessment, it is important to recognize that national ESGs are derived to provide estimates of the sediment concentrations of specific substances that are expected to protect communities of benthic organisms from chronic effects that are applicable across sediments—a goal that cannot be attained using other assessment methods.

Studies conducted to modify site-specific WQC have demonstrated that, if up-front planning with all stakeholders had occurred before beginning each site-specific study, the results of these studies could have been significantly improved (Brungs, 1992). Therefore, we strongly recommend that users of these guidelines for developing site-specific ESGs consult early, and closely, with the appropriate EPA Regional Office, Office of Science and Technology, and Office of Research and Development concerning the design and conduct of these procedures. In addition, experience with the use of the initial guidance for conducting site-specific WQC adjustments (U.S. EPA, 1983) has identified improvements in the procedures required to make the resultant site-specific criteria more appropriate and less costly to derive (U.S. EPA, 1994). EPA believes that application of these site-specific ESG procedures will identify improvements that will require modification over time. Because these procedures are

scientifically complex, it is important that they be conducted only by those who are well qualified and experienced.

1.3 Definition of Site of Concern and Resident Species at a Site

The aerial distribution of sediments that exhibit toxicity to benthic organisms, or exceed the national ESG, defines the site of concern. In the context of site-specific ESG derivation, the concept of site must be consistent with the requirements of the Resident Species Deletion/Substitution Procedure or the Bioavailability Procedure.

Derivation of a site-specific ESG based on species sensitivity differences requires identification of resident species expected to occur at the site. To identify the species expected to occur at the site where sediments exceed the ESG, a spatially larger area, as well as temporal changes in fauna, must be considered. The reason for this is that species may occur permanently, seasonally, or intermittently at the site and may be excluded from the site because of existing temporary conditions, including pollution. Therefore, the creation of a list of resident species might possibly require knowledge of those species occurring in adjacent water bodies or even in the entire ecological province. Species not occurring at the site, due for example to anthropogenic causes, must be included in a list of resident species because they would likely return if the pollutants or other conditions causing impacts were removed. Therefore, identification of resident species must include consideration of species found at the immediate site of concern over time, at other similar

sites, and so on, and may include entire biogeographic provinces. If the sediment is to be moved, the species resident at the site where sediments will be placed should be included as resident species.

The spatial extent of the site, as applied to the Bioavailability Procedure, includes only the area containing sediments that exceed the ESG. Of particular concern are those sediments from the site that exceed the ESG and are believed to be unique because of sediment characteristics or chemical form that may violate partitioning assumptions that are fundamental to the sediment guidelines.

In case site-specific ESGs are deemed necessary for purposes such as deriving permit limits and identifying causative chemicals for toxicity, EPA recommends preliminary site-specific evaluations prior to initiation of these site-specific modification procedures. For example, these procedures should not be used until the horizontal and vertical extent of sediments exceeding the ESG and the magnitude of the exceedance is determined. These monitoring studies can also be used to (1) determine if the partitioning of the chemical to sediments is as predicted by EqP (e.g., for nonionic organic chemicals) by comparing the ratio of the sediment concentration and the interstitial water concentration with the K_{OC} in the ESG document, (2) identify the chemical cause of the observed toxicity, or (3) determine if the toxicity of the sediment to the tested species is predicted by EqP theory. All of these can help determine if application of these site-specific ESG procedures will likely decrease or increase the national ESG.

Section 2

Procedures for Conducting Site-Specific ESG Modifications

2.1 Resident Species Deletion/Substitution Procedure

The Resident Species Deletion/Substitution Procedure is intended to result in a site-specific ESG that appropriately adjusts the national ESG when there are pertinent differences in the sensitivities of benthic organisms that occur at the site from those organisms used to derive the national ESG concentration. This procedure follows that found in "Appendix B Recalculation Procedure" of "Interim Guidance on Use of Water-Effect Ratios for Metals" (U.S. EPA, 1994).

2.1.1 *Rationale for Use of the Resident Species Deletion/Substitution Procedure*

This procedure is relevant for site-specific modification of national ESGs because (1) sensitive or insensitive benthic or water column species used to derive the national ESG may not occur at the site, (2) water column species or water column life-stages of species that also have benthic life-stages that do occur at the site may not be relevant to the ESG derivation, or (3) water column species and nonresident benthic species may be toxicological surrogates for taxonomically related but untested resident benthic species or benthic life-stages of water column species. The procedure considers the need to retain acute values for nonresident benthic species or resident and nonresident water column life-stages of benthic species as toxicological surrogates for taxonomically related but untested resident benthic species. The rules that permit deletion of data are intentionally restrictive because national databases often contain data for only a relatively small number of genera and deletion of data on nonresident species expected to represent the sensitivities of untested resident species must be avoided. Toxicity testing with resident benthic species may be needed to complete minimum database requirements for deriving guidelines. EPA encourages testing of resident benthic species to permit deletion of acute values for water column or nonresident benthic

species that serve as surrogates for untested resident benthic species. In addition, it is important to obtain data on recreationally important, commercially important, and endangered or threatened species found at the site.

For the purposes of this site-specific guidelines document, resident organisms that "occur at the site" are defined as those benthic species, genera, families, orders, classes, or phyla of organisms that would be expected to occur periodically or commonly at the location where sediments contain chemicals in excess of the ESG. However, note that determining the species expected to occur at the site will require expanding the definition of site. This includes organisms that would be expected to occur continually, seasonally, or intermittently; those now absent because of anthropogenic causes, and those that will be used as toxicological surrogates. Organisms absent because of physical changes, such as the impoundment of rivers, are not considered resident. Creation of a list of resident species will require the use of historical species lists for the site and, possibly, biological assessment databases from nearby reference sites. Enlisting the help of experts on local aquatic fauna is suggested to create the resident species list.

Use of this procedure may increase, decrease, or fail to change the national guideline value. If highly sensitive species are not present at the site, an increase in the guideline value is likely. If the number of acute values is decreased, the guideline value will likely decrease. Additional testing may reveal uniquely sensitive or resistant species that could lower or raise the guideline value. Because water column and benthic species have similar sensitivities (Di Toro et al., 1991; U.S. EPA, 2000c), deletion of acute values for certain water column species or life-stages, and replacement with newly obtained data on benthic organisms would, on the average, not be expected to markedly alter the guideline value.

2.1.2 Details of the Resident Species Deletion/Substitution Procedure

The basic principle of the Resident Species Deletion/Substitution Procedure is to permit deletion of all acute values for nonresident benthic species/life-stages and water column species/life-stages when acute values for all resident benthic species/life-stages in a family have been tested. While implementing this procedure, EPA encourages additional testing to overcome conservatism in rules that prohibit deletion of acute values that may be surrogates for acute values of untested resident benthic species in a family. Ten rules **MUST** be followed:

1. *Literature search:* A search **MUST** be conducted of the scientific literature and unpublished reports available since the date of the literature search for the ESG document to obtain all acceptable acute, chronic, and other toxicity data from water-only and sediment toxicity tests. Of particular interest are data such as those in Section 3, Section 4, or Appendix A of the chemical-specific ESG documents. The toxicity test results **MUST** be subject to rules for data acceptability found in Stephan et al. (1985), or subsequent guidance. The most important component of the review process is that a qualified reviewer **MUST** use good judgment in the review of data, experimental designs, and methods used. This process **MUST** include both published and unpublished data. Discarding good data needs to be avoided. Rejection of bad data is **REQUIRED**. The resultant acute toxicity dataset is the new "national database." The deletion process that follows pertains only to acute toxicity values, and the resultant database is termed the "site-specific database." (In the future, EPA intends to develop a database of toxicity test results that have been screened for applicability to sediment guidelines derivation. Until this database becomes available, those wishing to derive site-specific ESGs **MUST** conduct the literature search to obtain the new national database.)
2. *Applies to ALL data:* In all cases, deletion and substitution decisions **MUST** apply to the entire national database, not just to the data for sensitive species
3. *Resident benthic species in a class, order, or phylum have not been tested, but acute values for nonresident species in that class, order, or phylum are available.* If the national database contains acute values for benthic or water column life-stages of species in a class, order, or phylum from which resident benthic species have not been tested, the site-specific database **MUST** contain all data for species in that class, order, or phylum found in the national database.
4. *All resident benthic species in a family tested:* If a family contains one or more benthic genera that occur at the site, and if the national database contains every one of the resident species in these genera, the site-specific database **MUST** contain every one of these species that occur both at the site and in the national database, but **MUST NOT** contain any nonresident species in the genus or nonresident genera in the family.
5. *Not all resident benthic species in a family tested:* If a family contains one or more benthic genera that occur at the site, but the national database does **NOT** contain every one of the resident benthic species in each genus, the site-specific database **MUST** contain all of the species in the national database that are in that family.
6. *Benthic life-stages of all resident species in a family tested and water column life-stages of one or more of these resident species tested:* If a family that occurs at the site contains one or more genera with species having both benthic and water column life-stages, and if the national database contains acute values on the benthic life-stages for every one of the resident species and acute values for water column life-stages for one or more of these species, the site-specific database **MUST** contain every one of these acute values for the benthic life-stages of the species that occur at the site, but **MUST NOT** contain any acute values for nonresident benthic species or life-stages or acute values for the water column life-stages of any species in the family.
7. *Not all benthic life-stages of resident species in a family tested and nonresident benthic life-stages or water column life-stages of resident or nonresident species have been tested:* If one or more genera in a family that occurs at the site contain species with both benthic and water column life-stages, but the national database does **NOT** contain acute values on the benthic life-stages for every one of the resident species in all resident genera, the site-specific database **MUST** contain acute values for all benthic and water column life-stages for resident and nonresident species in all genera that are in the national database.

8. *Minimum data requirements.* If the site-specific database does not meet the minimum database requirements in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al., 1985), a site-specific sediment guideline value can not be derived and the national sediment quality guideline value applies to the site until additional acceptable toxicity tests are completed that meet the minimum data requirements
9. *Required and optional toxicity testing:* Toxicity tests **MUST** be conducted to complete minimum data requirements for deriving the WQC FCV or to ensure that data are available on at least one benthic species in each animal or plant class critical to the site and each resident benthic species, or an acceptable surrogate species, listed as threatened or endangered under Section 4 of the Endangered Species Act (ESA). Toxicity tests can be conducted on resident benthic species or benthic life-stages of resident species for which only water column life-stages have been tested to complete data requirements that permit deletion of data on nonresident benthic species and water column life-stages of either resident or nonresident species (see rules 3 to 7 above). It may be most helpful to repeat toxicity tests on four or more of the most sensitive resident genera in the national or site-specific databases using measured chemical concentrations and improved testing methodology to permit replacement of acute values from previously published tests.
10. *Critical species testing:* If data are not available for a critical resident benthic species that is threatened, endangered, commercially important, recreationally important, or ecologically important, data should be generated for that species or an acceptable surrogate species (see Stephan et al. [1985] for details on test requirements).

Step-by-step examples of the deletion procedure used to modify national WQC, a procedure not substantively different from this Deletion/Substitution Procedure for modifying national ESGs, are illustrated in Appendix B of the "Interim Guidance on Determination and Use of Water-Effect Ratios for Metals" (U.S. EPA, 1994). This deletion process is designed to ensure the following.

 - a. Each benthic species, or benthic life-stage of a species that has both benthic and water column life-stages, that occurs both in the national dataset and at the site also occurs in the site-specific dataset.
 - b. Each species having a benthic life-stage that occurs at the site, but does not occur in the national dataset, is represented in the site-specific dataset by ALL species in the site-specific dataset that are in the same genus.
 - c. Each genus having species with a benthic life-stage that occurs at the site, but does not occur in the national dataset, is represented in the site-specific dataset by ALL genera in the national dataset that are in the same family
 - d. Each order, class, and phylum that occurs both in the national dataset and at the site is represented in the site-specific dataset by one or more benthic or water column species in the national dataset that are closely related to a species that occurs at the site.
 - e. Testing is encouraged or required to add new acute toxicity data to the site-specific dataset on critical resident benthic species that are threatened, endangered, commercially important, recreationally important, or ecologically important, or to permit deletion of data on nonresident benthic species.

2.1.3 Derivation of the Site-Specific ESG

Following the Deletion/Substitution Procedure above, the guidelines for the derivation of a FCV (Stephan et al., 1985) must be applied to the site-specific database. Species mean acute values (SMAVs) and genus mean acute values (GMAVs) must be calculated. If minimum database requirements are met, except those that require water column species, a site-specific final acute value (FAV_{SS}) is calculated. If an acute value for a critical resident benthic species that is threatened, endangered, commercially important, recreationally important, or ecologically important is lower than the FAV, this value becomes the FAV. Finally, the FAV is divided by the final acute-chronic ratio (FACR) from the ESG document, or the new site-specific FACR (FACR_{SS}) derived using new chronic data from the literature search, to derive the site-specific FCV (FCV_{SS}). Acute-chronic ratios (ACRs) for sensitive benthic species do not differ from those of the entire WQC database of acute-chronic ratios (U.S. EPA, 2000c,e), therefore, the deletion procedure does not apply to the chronic toxicity database for a substance for which an ESG is available.

The site-specific ESG, on an organic carbon basis, is the product of the K_{OC} from the ESG document and the FCV_{SS}

$$ESG_{OC,SS} = K_{OC} FCV_{SS} \quad (2-1)$$

This $ESG_{OC,SS}$ and the procedures in Section 5 of the relevant ESG document should be used to derive the 95% confidence intervals.

All steps in the derivation of a site-specific ESG must be documented in a report that includes a table listing (1) all species and their life-stages used to derive SMAVs, (2) all species and life-stages deleted, (3) test conditions of the SMAV and GMAV data used for calculation, and (4) references for the source of the acute values. This table should be similar to Appendix A in the ESG documents. The new calculated FAV_{SS} , $FACR_{SS}$, FCV_{SS} , and $ESG_{OC,SS}$ should appear after the tabular presentation of toxicity data. All toxicity data on all aquatic resident animal and plant species, especially critical resident benthic species that are threatened, endangered, commercially important, recreationally important, or ecologically important, must be listed to permit comparisons between their sensitivities and the FAV or FCV . All other species known to be resident to the site and the source of this information must also be listed.

2.2 Bioavailability Procedure

The Bioavailability Procedure is intended to result in a site-specific ESG that appropriately replaces the national ESG when there are pertinent differences in the bioavailability of the chemical in the sediment from the site, due to partitioning phases in the sediment, in addition to organic carbon, or the presence in the sediment of undissolved chemical. These alternate partitioning phases may include, but not be limited to, interstitial dissolved organic carbon (DOC), pure chemical, or soot carbon. This approach assumes that the "true" bioavailable concentration can be reasonably measured or estimated as "freely-dissolved" chemical in the interstitial water, which can then be compared with the WQC FCV . Sediments in which the freely-dissolved interstitial water concentration is less than the WQC FCV would not be expected to cause toxicity to benthic organisms and are acceptable for maintaining the presence of the benthic community.

2.2.1 Rationale for Use of the Bioavailability Procedure

EPA's sediment guidelines for nonionic organic chemicals are based on the EqP model. This model uses a two-phase approach: particulate-associated chemical and dissolved interstitial chemical, where the total concentration in sediment equals the concentration in the particulate phase plus the concentration freely-dissolved in interstitial water. If alternate phases exist in a sediment, it is possible that the EqP model for sediment guidelines may not directly apply. In these cases, the toxicity of the sediment cannot be predicted from the two-phase carbon-normalized sediment concentrations and the K_{OC} because, in addition to organic carbon, combustion particles, pure chemical, or other properties of the sediments at the site may alter bioavailability. For these sediments, site-specific criteria modification using the Bioavailability Procedure is warranted.

The Bioavailability Procedure compares the bioavailable, freely-dissolved interstitial water concentration with the WQC FCV found in the sediment guideline document, or the site-specific final chronic value derived using the Resident Species Deletion/Substitution Procedure above. If the interstitial water concentrations are below the WQC FCV , the concentration of the chemical is below the site-specific ESG. The three approaches EPA recommends for estimating or measuring the freely-dissolved chemical concentration in interstitial water require procedures appropriate for obtaining and chemically analyzing interstitial water. The approaches assume that the chemical is distributed into three phases: freely-dissolved, DOC-associated, and particulate. The Bioavailability Approach assumes that the use of the two-phase based K_{OC} in calculating the freely-dissolved concentration from sediment concentrations is not appropriate for this sediment, and furthermore, that the bioavailable concentrations can be determined directly from an interstitial water sample. The analytical procedures presented below employ the best presently available technology for obtaining interstitial water, chemically analyzing interstitial water chemical concentrations, and estimating or measuring the freely-dissolved concentration of the chemical.

2.2.2 Details of the Bioavailability Procedure

The problem of adequately collecting and processing interstitial water samples is well documented (Adams, 1991; Schults et al., 1992; Ankley and Schubauer-Berigan, 1994; ASTM, 1994; Ozretich and Schults, 1998). Artifacts from the procedures can preclude accurate determination of interstitial water contaminant concentrations. The following procedures are recommended to minimize effects of interstitial water sample collection and processing for nonionic organics.

2.2.2.1 Sampling Interstitial Water

In general, centrifugation without subsequent filtration results in the highest concentrations of metals and nonionic organic compounds in interstitial water from fine-grained, high water content sediment. Because the objective of centrifugation is to obtain interstitial water containing material smaller in diameter than that which would pass through a $0.45\ \mu\text{m}$ filter (i.e., only the "soluble fraction"), any combination of gravitational force (speed with effective radius) and time that would settle the particles of greater effective diameter to the sediment-interstitial water interface would be acceptable. For example, the following recommended procedure resulted in 25 to 60 mL of clear interstitial water from several industrialized waterways including the Lauritzen Channel in northern San Francisco Bay (Lee et al., 1994; Swartz et al., 1994). A 150 g portion of wet sediment in a 150 mL glass centrifuge bottle (Corex, Corning®) is spun at 5,000 rpm ($2,590\text{--}4,080 \times g$) in a fixed angle rotor (GSA, Sorvall®) for 90 min at 4°C to obtain maximum volumes. When completed, the centrifuge bottle is back-lighted and the interstitial water is gently aspirated through Teflon® tubing (drawn to a fine point) and placed deep into the bottle next to the sediment/water interface. The interstitial water passes through a stainless steel needle directly into a glass vial. This procedure has been shown to reduce losses of organic constituents (Ozretich and Schults, 1998). At this point, subsamples can be taken for measurement of DOC (~3 mL). The DOC-associated components (12–40 mL) (Landrum et al., 1984; Ozretich et al., 1995) and the remaining interstitial water (12–40 mL) can be extracted in the receiving vial for the determination of the total chemical concentration (freely-dissolved fraction plus the fraction bound to dissolved DOC material). Collecting and subsampling the interstitial water must be done within 2 hours to avoid complications from the potential formation of *de novo* particles from oxidation of reduced iron. It is clear that cleanly sampled interstitial water is important, as the presence of a

particle of sediment could result in erroneously high concentrations; on the other hand, if the time periods before extractions are long or filtering and excessive sample handling has occurred, erroneously low concentrations would result as the chemicals are sorbed to surfaces.

2.2.2.2 Quantification of Dissolved and DOC-Associated Phases

Once an adequate interstitial water sample has been obtained, the quantity of contaminant present must be accurately determined. Liquid-liquid (L-L) extraction methods are routinely used to extract total water samples and the DOC-associated fraction. Commonly used L-L procedures (U.S. EPA, 1986) for total water samples include the use of separatory funnels (Method 3510C) and, when emulsions are encountered, continuous extraction (Method 3520C). PAHs and chlorinated pesticide compounds are typically quantified in 1 mL extracts from 1 L samples by GC/MS (Method 8270C) in the scan mode with quantitation limits of $10\ \mu\text{g/L}$ (PAHs), which exceeds the solubility of many of the higher molecular weight compounds for which these combined methods were developed. Clearly, the recommended volumes and mass spectrometer operational conditions of these standard procedures are not adequate to quantify the same compounds in easily obtained volumes of interstitial water at concentrations near their WQC FCVs. Alternatively, the gentle L-L extraction procedure used for small volumes of interstitial water is recommended (Ozretich et al., 1995), because it is conceptually similar to continuous extraction in providing long solvent-sample contact time while eliminating emulsions. In addition, it uses fewer extraction solvents and no elaborate, hard-to-clean glassware. Because the need to do a site-specific determination of freely-dissolved interstitial water concentrations is related to concerns regarding the applicability of carbon-normalized concentrations of a specific compound, the mass spectrometer need not be operated in the scanning mode, but may be optimized only for the mass fragmentation ions of the compound of concern by operating in the selected ion mode, and limiting the ions to 2–5 with maximum dwell times, as is used for chlorinated dioxins and furans (Method 8280) (U.S. EPA, 1992). By combining these mass spectrometer modifications with smaller sample sizes reduced to smaller volumes (50–250 μL) but larger injection volumes (2–5 μL ; instrument dependent), sample quantitation limits on the order of 10–50 ng/L can be achieved (Ozretich et al., 1995).

2.2.2.3 Calculating the Freely-Dissolved, Bioavailable Concentration

The bioavailable interstitial water concentration of a chemical can be determined in the following three ways.

1. It can be assumed that the total interstitial water concentration (C_{IW}) for a nonionic organic chemical with a low to intermediate octanol-water partition coefficient (K_{OW}) value is equivalent to the dissolved concentration; that is, the freely-dissolved interstitial water concentration equals the total dissolved interstitial water concentration. However, this approach may be problematic because high concentration of DOC can be present in interstitial water. Nonionic organics are known to bind to this material, causing a reduction in their bioavailability. Therefore, a L-L extraction of interstitial water would contain the freely-dissolved and the DOC-associated chemical, overestimating the true bioavailable concentration. The magnitude of the overestimate would depend on the affinity of the DOC for the chemical of interest. This affinity is represented by the partition coefficient K_{DOC} , which is the ratio of the chemical concentration bound to the DOC to the freely-dissolved interstitial water concentration.
2. It can be determined that the freely-dissolved interstitial water concentration is the difference between the total interstitial water concentration and the DOC-associated concentration. This method depends on the DOC-associated concentration being operationally defined and limited by the methodology (e.g., the separation of total and bound fractions by C18 columns) (Landrum et al., 1984; Ozretich et al., 1995). However, use of this procedure doubles the number of samples that need to be taken and analyzed, and may require monitoring of DOC retention (Ozretich et al., 1995). When using a similar procedure to separate the DOC-associated chemical, the freely-dissolved concentration can be directly measured (Burgess et al., 1996). This approach should be used only if acceptable concentration mass balances (approximately 90%) of the DOC, dissolved, and total chemical are available (R.M. Burgess, U.S. EPA, Narragansett, RI, personal communication).
3. It can be calculated from the total concentration using the DOC concentration and the K_{DOC} of the

compound from Equations 2-2 and 2-3, where the freely-dissolved (bioavailable) interstitial water chemical concentration is

$$C_d = C_{IW} / (DOCK_{DOC} + 1) \quad (2-2)$$

and the percentage of the total compound that is freely-dissolved is

$$\%C_d = 1 / (DOCK_{DOC} + 1) \times 100 \quad (2-3)$$

This method depends on determination of DOC (kg/L) and K_{DOC} . Determining the concentration of DOC in water is routine. However, identifying valid K_{DOC} values is problematic at this time.

Generally, it would be inappropriate to use K_{OC} to represent the partition coefficient of a chemical to DOC material in calculating freely-dissolved concentrations because particulate organic matter, represented by K_{OC} , is generally described as very nonpolar and insoluble in interstitial water. Conversely, dissolved or DOC, represented by K_{DOC} , is relatively more polar and soluble in interstitial water (Chiou et al., 1986). Fundamental differences in solubility of these types of organic carbon in sediments will most likely also cause differences in the magnitude of their respective partition coefficients for a given chemical. Therefore, they should not be used interchangeably.

When available, K_{DOC} values have been plotted versus K_{OW} values for chemicals with $\log_{10} K_{OW}$ values <6.5, and a generally linear relationship is observed (Ozretich et al., 1995; Burgess et al., 1996). For example, Ozretich et al. (1995), using the C-18 separation technique, found the following relationship (Equation 2-4) between published K_{OW} and measured K_{DOC} values of multiple PAHs and chlorinated hydrocarbons that were placed in interstitial water and allowed to equilibrate with unfractionated DOC.

$$\log_{10} K_{DOC} = 0.907 \log_{10} K_{OW} - 0.751 \quad (2-4)$$

Using this equation, computed K_{DOC} values from the endrin and dieldrin ESG documents were compared with K_{OC} values (Table 2-1), and the percentage of the total compound that is freely-dissolved, calculated using Equation 2-3, was determined for a range of DOC concentrations that are likely to be encountered in interstitial water (Table 2-2). The greatest percentage of a guideline chemical that would be bound to DOC material using K_{DOC} is approximately 50% for dieldrin

($\log_{10} K_{OW} = 5.37$) at 70 mg DOC/L. Using K_{OC} in Equation 2-4, approximately 93% of dieldrin would be computed to be bound at this DOC level. Therefore, using the total concentrations as bioavailable would overestimate the freely-dissolved concentration by a factor of 14 if partitioning were assumed to be more soil-like using K_{OC} in Equation 2-2 or by a factor of 2 using K_{DOC} .

For the purposes of this document, it is recommended that Equation 2-4 be used with Equation 2-2 to calculate the C_d , because K_{DOC} is more representative of binding to dissolved DOC material than K_{OC} .

2.2.3 Derivation of the Site-Specific ESG

This calculated or measured C_d is compared with the WQC FCV from the individual ESG documents. If the freely-dissolved interstitial water concentration is less than the FCV, toxicity would not be expected and the sediment would be acceptable for maintaining the presence of benthic organisms. Alternatively, the interstitial water concentration can be compared with the FCV derived using the Resident Species Deletion/Substitution Approach.

Table 2-1. Computed organic carbon-normalized partition coefficients

Compound	$\log_{10} K_{OW}^a$	$\log_{10} K_{DOC}^b$	$\log_{10} K_{OC}^c$
Endrin	5.06	3.84	4.97
Dieldrin	5.37	4.12	5.28

^aFrom corresponding ESG documents

^bDerived using Equation 2-4.

^cFrom corresponding ESG documents using: $\log_{10} K_{OC} = 0.983 \times \log_{10} K_{OW} + 0.00028$

Table 2-2. Solutions to Equation 2-3 using K_{DOC} values computed from Equation 2-4

DOC (mg/L)	Endrin (% free)	Dieldrin (% free)
0	100	100
5	97	94
10	94	88
15	91	83
20	88	79
25	85	75
30	83	72
40	78	65
50	74	60
60	71	56
70	67	52

Section 3

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